PREFACE

Donor Acceptor (D-A) interaction first proposed by Mulliken is now recognised to play a key role in many chemical and biological processes Many studies exist on spectral thermodynamic and other aspects of a large number of electron donor acceptor com plexes Primarily electronic absorption spectroscopy has been used since n donors and I_2 mixed in non polar solvents have a characteristic charge transfer(C-T) band in the visible region However similar n σ complexes of other halogens viz Br_2 Cl_2 and interhalogens BrCl and ICl could not be studied by UV absorption spectroscopy because the C-T bands are shifted to the vacuum UV region Eventhough extensive spectroscopic studies on D A complexes exist in the literature exact orbitals involved in the complex formation extent of charge transfer orbitals responsible for the C T excitations blue shifts in the absorption of the acceptor molecules and such details are not available even for the most well known diethy ether I_2 complex UV photoelectron spectroscopy (UVPES) provides direct information on the orbital ionization energies and electron energy loss spectroscopy (EELS) provides excitation energies in the visible as well as vacuum UV region Further, these two experimental techniques are amenable to study molecular complexes in gaseous phase Considerably more information on molecular interactions can be obtained when the studies are complemented by quantum chemical calculations Precise geometry of the complexes extent of charge transfer and nature of orbital interactions can be determined In this thesis electron spectroscopic studies of D-A complexes and hydrogen bonded complexes and their ab-initio MO calculations are presented

In the introduction chapter an overview of the various molecular interactions meth ods employed to study D A complexes and hydrogen bonded complexes are presented Advantage of UVPES and EELS over other spectroscopic techniques is discussed Ab intio MO calculations on D A complexes information which can be obtained from the

calculations and their limitations are also presented

In chapter 2 design and fabrication of a high resolution electron energy loss spectrometer to study electronic excitations of molecules is described The spectrometer consists of a 180 hemispherical electron energy monochromator molecule-electron beam collision chamber 180 hemispherical electron energy analyser a channel electron multiplier for electron detection associated with ratemeter and digital data acquisition system Resolution of the spectrometer is about 200 meV at a primary beam energy of 40 eV Performance of the spectrometer is demonstrated by recording EELS of O_2 and N_2 in air HCl and NH_3 molecules Higher resolution of the spectrometer is confirmed from the vibrational progression observed for the first X→A transition in ammonia molecule

In chapter 3 study of electronic transitions in halogens Cl_2 Br_2 and I_2 and tetrahalides $TiCl_4$ and $GeCl_4$ by EELS is presented The electronic transitions observed here are assigned and interpreted with the values obtained from ab-initio MO calculation quantum defect calculations and in some systems with optical absorption studies Combining the electron states of occupied levels from UVPES and excitation energies from EELS energy level diagrams are constructed for all these molecules

UVPES and EELS studies of D A complexes and their ab-initio MO studies are presented in chapter 4 Ultraviolet photoelectron spectra of gas-phase complexes formed by Br_2 $TiCl_4$ ICl with donors diethyl ether and diethyl sulphide have been obtained The orbital ionization energies are assigned using ab initio MO calculations The key spectral features are assigned to the highest occupied molecular orbitals derived from acceptor and the donor molecules whose ionization energies are shifted to lower and higher binding energies respectively For example in diethyl ether Br_2 (D-A) complex lone pair orbitals of oxygen are shifted to higher binding energy by about 0 2 eV and those of Br_2 orbitals to lower energy by 0 3 eV All-electron and effective core potential calculations

have been done to get a minimum energy geometry structure Charge transfer in the case of ether is from the σ type lone pair of oxygen whereas in the diethyl sulphide it is from the π type lone pair The nature and magnitude of shifts in the orbitals are found to be comparable to the computed binding energy and quantum of charge transfer EELS of charge transfer complexes of I_2 Br_2 Cl_2 and $TiCl_4$ have been obtained The C T bands observed in the case of diethyl ether and the halogens are due to the excitation from the σ type lone pair of oxygen to the σ_u of the halogens From the UVPES and EELS studies complete energy level diagram of the complexes of I_2 Br_2 Cl_2 with diethyl ether have been obtained Ab-initio MO calculations on complexes of ICl and IBr with donors like diethyl ether diethyl sulphide and trimethylamine have been investigated The ICl complexes are found to be stronger of all the halogens and interhalogen complexes Complex of benzene with bromine where benzene acts as a donor is studied by means of photoelectron spectroscopy Theoretical investigation of the complexes of benzene with halogens iodine bromine and interhalogens ICl and IBr have also been done The complexes are of weak $\pi \rightarrow \sigma$ type between benzene and the acceptor

In Chapter 5 studies on electron states of benzene – – –HCl toluene – – –HCl H_2S – – –HCl and diethyl sulphide – – –HCl hydrogen bonded complexes by Molec ular beam UV photoelectron spectroscopy is reported The vertical ionization energies observed in the benzene – – –HCl complex at 10 84 and 12 10 eV have been assigned to Π C_6H_6 and n_{Cl} orbitals respectively While the Π C_6H_6 orbital in the complex is shifted by 1 57 eV to higher binding energy the n_{Cl} MO is shifted by 0 63 eV to lower binding energy with reference to the corresponding free benzene and HCl molecules Ab initio MO calculations confirm these assignments Toluene – – –HCl complex has also been studied The larger shifts in the Π(1 90 eV) and n_{Cl}(0 88 eV) orbital energies in the toluene – – – HCl complex compared to those of benzene – – –HCl complex are

consistent with stronger Π hydrogen bonding in the case of toluene HeI photoelectron spectrum of the H_2S – – –HCl complex shows two vertical ionization energies at 10 9 and 12 1 eV Ab- initio MO calculations reveal that these features are due to the sulphur and chlorine lone pair ionizations respectively Calculations and the experiment show that the ground ionic state is repulsive The first excited ionic state is strongly bound The photoelectron spectrum of diethyl sulphide – – –HCl shows higher shifts of sulphur and Cl lone pair orbitals indicating stronger hydrogen bonding then H_2S – – –HCl Ab-initio MO calculations on this complex predicted a binding energy of 5 8 kcal/mole at MP2/6 31G level whereas that of H_2S – – –HCl at the same level is 4 8 kcal/mole

The focus of this thesis is on the minimum energy geometry of the complexes nature of the orbital involved in the D A and hydrogen bond formation extent of charge transfer electron states involved in the C-T absorption band blue shifts occuring in the visible and vacuum UV regions of halogens due to complex formation Reasonable answersto all these points have been obtained

The work described in this thesis has been carried out by the candidate as part of the Ph D training program He hopes that the work presented here is a worthwhile contribution to the area of donor acceptor interactions